Claims

1. A proton-conducting polymer membrane comprising polymers containing sulfonic acid groups, obtainable by a process comprising the steps of
A) mixing vinyl-containing sulfonic acid with one or more aromatic tetraamino compounds with one or more aromatic carboxylic acids, their esters, their acid halides or their acid anhydrides, containing at least two acid groups per carboxylic acid monomer, and/or
mixing vinyl-containing sulfonic acid with one or more aromatic and/or heteroaromatic diaminocarboxylic acids, their esters, their acid halides or their acid anhydrides,
B) heating the mixture obtainable according to step A) under inert gas to temperatures of up to 350°C, to form polyazole polymers,
C) applying a layer to a support, using the mixture according to step A) and/or B),
D) polymerizing the vinyl-containing sulfonic acid present in the sheetlike structure obtainable according to step C).

2. The membrane of claim 1, characterized in that as aromatic tetraamino compounds 3,3',4,4'-tetraaminobiphenyl, 2,3,5,6-tetraaminopyridine, 1,2,4,5-tetraaminobenzene, 3,3',4,4'-tetraaminodiphenyl sulfone, 3,3',4,4'-tetraaminodiphenyl ether, 3,3',4,4'-tetraaminobenzophenone, 3,3',4,4'-tetraaminodiphenyl methane and 3,3',4,4'-tetraaminodiphenyldimethyl methane is used.

3. The membrane of claim 1 or 2, characterized in that as aromatic carboxylic acids isophthalic acid, terephthalic acid, phthalic acid, 5-hydroxyisophthalic acid, 4-hydroxyisophthalic acid, 2-hydroxyterephthalic acid, 5-aminoisophthalic acid, 5-N,N-dimethylaminoisophthalic acid, 5-N,N-diethylaminoisophthalic acid, 2,5-dihydroxyterephthalic acid, 2,5-dihydroxyisophthalic acid, 2,3-dihydroxyisophthalic acid, 2,3-dihydroxyphthalic acid, 2,4-dihydroxyphthalic acid, 3,4-dihydroxyphthalic acid; 3-fluorophthalic acid, 5-fluoroisophthalic acid, 2-fluoroterephthalic acid, tetrafluorophthalic acid, tetrafluoroisophthalic acid, tetrafluoroterephthalic acid, 1,4-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, diphenic acid, 1,8-dihydroxynaphthalene-3,6-dicarboxylic acid, diphenyl ether 4,4'-dicarboxylic acid, benzophenone-4,4'-dicarboxylic acid, diphenyl sulfone 4,4'-dicarboxylic acid, biphenyl-4,4'-dicarboxylic acid, 4-trifluoromethylphthalic acid, 2,2-bis(4-carboxyphenyl)hexafluoropropane, 4,4'-stilbenedicarboxylic acid,

4-carboxycinnamic acid, or their C1-C20 alkyl esters, their C5-C12 aryl esters, their acid anhydrides or their acid chlorides are used.

4. The membrane of one or more of the preceding claims, characterized in that as aromatic carboxylic acid tricarboxylic acids, their C1-C20 alkyl esters, their C5-C12 aryl esters, their acid anhydrides or their acid chlorides or tetracarboxylic acids, their C1-C20 alkyl esters, their C5-C12 aryl esters, their acid anhydrides or their acid chlorides are used.

5. The membrane of claim 4, characterized in that as aromatic carboxylic acid 1,3,5-benzenetricarboxylic acid (trimesic acid); 2,4,5-benzenetricarboxylic acid (trimellitic acid); (2-carboxyphenyl)iminodiacetic acid, 3,5,3'-biphenyl-tricarboxylic acid; 3,5,4'-biphenyltricarboxylic acid 2,4,6-pyridinetricarboxylic acid, benzene-1,2,4,5-tetracarboxylic acids; naphthalene-1,4,5,8-tetracarboxylic acids, 3,5,3',5'-biphenyltetracarboxylic acids, benzophenonetetracarboxylic acid, 3,3',4,4'-biphenyltetracarboxylic acid, 2,2',3,3'-biphenyltetracarboxylic acid, 1,2,5,6-naphthalenetetracarboxylic acid and/or 1,4,5,8-napththalenetetracarboxylic acid are used.

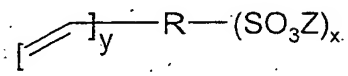
6. The membrane of claim 4, characterized in that the amount of tricarboxylic acid and/or tetracarboxylic acids is between 0 and 30 mol%, preferably 0.1 and 20 mol%, in particular 0.5 and 10 mol%, based on dicarboxylic acid used.

7. The membrane of claim 1, characterized in that as heteroaromatic carboxylic acids heteroaromatic dicarboxylic acids, heteroaromatic tricarboxylic acids and/or heteroaromatic tetracarboxylic acids which contain at least one nitrogen, oxygen, sulfur or phosphorus atom in the aromatic moiety are used.

8. The membrane of claim 7 characterized in that pyridine- pyridine-2,5-di-carboxylic acid, pyridine-3,5-dicarboxylic acid, pyridine-2,6-dicarboxylic acid, pyridine-2,4-dicarboxylic acid, 4-phenyl-2,5-pyridinedicarboxylic acid, 3,5-pyrazoledicarboxylic acid, 2,6 pyrimidinedicarboxylic acid, 2,5-pyrazine-dicarboxylic acid, 2,4,6-pyridinetricarboxylic acid, benzimidazole-5,6-di-carboxylic acid, and their C1-C20 alkyl esters or C5-C12 aryl esters, or their acid anhydrides or their acid chlorides are used.

9. The membrane of claim 1, characterized in that as aromatic diaminocarboxylic acid diaminobenzoic acid and/or the mono- and dihydrochloride derivatives thereof are used.

10. The membrane of claim 1, characterized in that the mixture prepared in step A) comprises compounds of the formula



in which

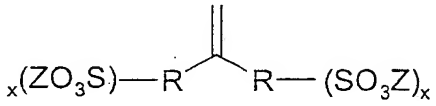
R is a bond, a C1-C15 alkyl group, C1-C15 alkoxy group, ethyleneoxy group or C5-C20 aryl or heteroaryl group, it being possible for the above radicals to be substituted in turn by halogen, -OH, COOZ, -CN, NZ_2,

Z independently at each occurrence is hydrogen, C1-C15 alkyl group, C1-C15 alkoxy group, ethyleneoxy group or C5-C20 aryl or heteroaryl group, it being possible for the above radicals to be substituted in turn by halogen, -OH, -CN, and

x is an integer 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10,

y is an integer 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10

and/or of the formula



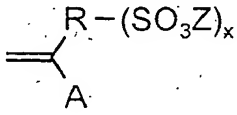
in which

R is a bond, a C1-C15 alkyl group, C1-C15 alkoxy group, ethyleneoxy group or C5-C20 aryl or heteroaryl group, it being possible for the above radicals to be substituted in turn by halogen, -OH, COOZ, -CN, NZ_2,

Z independently at each occurrence is hydrogen, C1-C15 alkyl group, C1-C15 alkoxy group, ethyleneoxy group or C5-C20 aryl or heteroaryl group, it being possible for the above radicals to be substituted in turn by halogen, -OH, -CN, and

x is an integer 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10,

and/or of the formula



in which

A is a group of the formulae $COOR^2$, CN, $CONR^2_2$, OR^2 and/or R^2,

in which R^2 is hydrogen, a C1-C15 alkyl group, C1-C15-alkoxy group, ethyleneoxy group or C5-C20 aryl or heteroaryl group, it being

possible for the above radicals to be substituted in turn by halogen, -OH, COOZ, -CN, NZ_2,

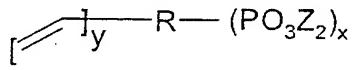
R is a bond, a divalent C1-C15 alkylene group, divalent C1-C15 alkyleneoxy group, such as divalent ethyleneoxy group or C5-C20 aryl or heteroaryl group, it being possible for the above radicals to be substituted in turn by halogen, -OH, COOZ, -CN, NZ_2,

Z independently at each occurrence is hydrogen, C1-C15 alkyl group, C1-C15 alkoxy group, ethyleneoxy group or C5-C20 aryl or heteroaryl group, it being possible for the above radicals to be substituted in turn by halogen, -OH, -CN, and

x is an integer 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10.

11. The membrane of claim 1, characterized in that the mixture prepared in step A) and/or step B) comprises vinyl-containing phosphonic acid.

12. The membrane of claim 11, characterized in that the mixture prepared in step A) and/or step B) comprises compounds of the formula



in which

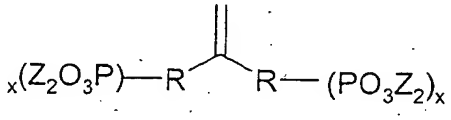
R is a bond, a C1-C15 alkyl group, C1-C15 alkoxy group, ethyleneoxy group or C5-C20 aryl or heteroaryl group, it being possible for the above radicals to be substituted in turn by halogen, -OH, COOZ, -CN, NZ_2,

Z independently at each occurrence is hydrogen, C1-C15 alkyl group, C1-C15 alkoxy group, ethyleneoxy group or C5-C20 aryl or heteroaryl group, it being possible for the above radicals to be substituted in turn by halogen, -OH, -CN, and

x is an integer 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10,

y is an integer 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10

and/or of the formula



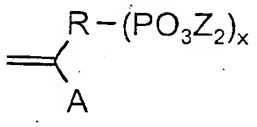
in which

R is a bond, a C1-C15 alkyl group, C1-C15 alkoxy group, ethyleneoxy group or C5-C20 aryl or heteroaryl group, it being possible for the above radicals to be substituted in turn by halogen, -OH, COOZ, -CN, NZ_2,

Z independently at each occurrence is hydrogen, C1-C15 alkyl group, C1-C15 alkoxy group, ethyleneoxy group or C5-C20 aryl or heteroaryl group, it being possible for the above radicals to be substituted in turn by halogen, -OH, -CN, and

x is an integer 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10,

and/or of the formula



in which

A is a group of the formulae $COOR^2$, CN, $CONR^2_2$, OR^2 and/or R^2, in which R^2 is hydrogen, a C1-C15 alkyl group, C1-C15-alkoxy group, ethyleneoxy group or C5-C20 aryl or heteroaryl group, it being possible for the above radicals to be substituted in turn by halogen, -OH, COOZ, -CN, NZ_2,

R is a bond, a divalent C1-C15 alkylene group, divalent C1-C15 alkyleneoxy group, such as ethyleneoxy group or divalent C5-C20 aryl or heteroaryl group, it being possible for the above radicals to be substituted in turn by halogen, -OH, COOZ, -CN, NZ_2,

Z independently at each occurrence is hydrogen, C1-C15 alkyl group, C1-C15 alkoxy group, ethyleneoxy group or C5-C20 aryl or heteroaryl group, it being possible for the above radicals to be substituted in turn by halogen, -OH, -CN, and

x is an integer 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10.

13. The membrane of claim 10 or 11, characterized in that the weight ratio of vinyl-containing phosphonic acid to vinyl-containing sulfonic acid is in the range from 1:100 to 99:1.

14. The membrane of claim 1, characterized in that in step D) monomers capable of crosslinking which contain at least two carbon-carbon double bonds are polymerized.

15. The membrane of claim 1, characterized in that the polymerization according to step D) is brought about by means of a substance capable of forming free radicals.

16. The membrane of claim 1, characterized in that the polymerization according to step D) takes place by irradiation of IR or NIR light, UV light, ß, γ and/or electron beams.

17. The membrane of claim 1, characterized in that the mixture produced in step A) and/or step B) comprises dissolved, dispersed and/or suspended polymer.

18. The membrane of claim 1, characterized in that in step C) a layer having a thickness between 20 and 4000 µm, preferably between 30 and 3500 µm, in particular between 50 and 3000 µm is produced.

19. The membrane of claim 1, characterized in that the membrane formed after step D) has a thickness of between 15 and 3000 µm, preferably between 20 and 2000 µm, in particular between 20 and 1500 µm.

20. An electrode having a proton-conducting polymer coating based on polyazoles obtainable by a process comprising the steps of

A) mixing one or more aromatic tetraamino compounds with one or more aromatic carboxylic acids, their esters, their acid halides or their acid anhydrides, containing at least two acid groups per carboxylic acid monomer, or mixing one or more aromatic and/or heteroaromatic diaminocarboxylic acids, their esters, their acid halides or their acid anhydrides, and with vinyl-containing sulfonic acid,

B) heating the mixture obtainable according to step A) under inert gas to temperatures of up to 350°C, to form polyazole polymers,

C) applying a layer to an electrode, using the mixture according to step A) and/or B),

D) polymerizing the vinyl-containing sulfonic acid.

21. The electrode of claim 19, wherein the coating has a thickness of between 2 and 3000 µm, preferably between 3 and 2000 µm, in particular between 5 and 1500 µm.

22. A membrane electrode assembly comprising at least one electrode and at least one membrane of one or more of claims 1 to 18.

23. A membrane electrode assembly comprising at least one electrode of claims 19 or 20 and at least one membrane of one or more of claims 1 to 18.

24. A fuel cell comprising one or more membrane electrode assemblies of claim 21 or 22.

25. A process for producing proton-conducting polymer membranes comprising polymers containing sulfonic acid groups which comprises the steps of

A) mixing one or more aromatic tetraamino compounds with one or more aromatic carboxylic acids, their esters, their acid halides or their acid anhydrides, containing at least two acid groups per carboxylic acid monomer, or mixing one or more aromatic and/or heteroaromatic diaminocarboxylic acids, their esters, their acid halides or their acid anhydrides, and with vinyl-containing sulfonic acid,

B) heating the mixture obtainable according to step A) under inert gas to temperatures of up to 350°C, to form polyazole polymers,

C) applying a layer to a support, using the mixture according to step A) and/or B),

D) polymerizing the vinyl-containing sulfonic acid.